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KINETICS OF THE OXIDATION OF MAGNESIUM FLUORIDE

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Research and Development

UCRL-9821
UC-4 Chemistry
TID-4500 (16th Ed.)

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

KINETICS OF THE OXIDATION OF MAGNESIUM FLUORIDE

Donald R. Messier

(M. S. Thesis)

August 15, 1961

Printed in USA. Price 75 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

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ABSTRACT

The kinetics of the reaction between MgF_2 and water vapor were studied in the temperature range from 950 to 1100°C. Determinations on powdered, sintered polycrystalline, and single-crystal specimens yielded different activation energies. The differences were attributed to differences in microstructure among the several specimen types.

Reaction rates were determined by measuring weight loss with a silica helix and cathetometer arrangement. The reaction was carried out in a flowing atmosphere of argon which possessed a known water-vapor partial pressure.

With all sample types, the reaction was interface-controlled. After the attainment of steady-state conditions, a 2/3-order rate law was followed.

Activation energies of 25, 56.1±6, and 42.3±5 kcal per mole were obtained for the powdered, sintered polycrystalline, and single-crystal specimens, respectively. The single-crystal value agreed with the heat of reaction of 43.8 kcal. per mole, indicating that the rate-controlling step was the chemical reaction itself. The low value for the powdered specimens was a result of area changes caused by sintering. The structure of the product layer on the presintered polycrystalline specimens was such that it provided greater impedance to gas flow than the single-crystal product layer. Consequently, a greater reaction-rate temperature coefficient and higher activation energy resulted.

I. INTRODUCTION

Some preliminary work leading to this investigation was concerned with the reaction of magnesium fluoride and alumina in air to form spinel:

$$1/2\,O_2(g) + Al_2O_3(s) + MgF_2(s) \rightarrow MgO\text{-}Al_2O_3(s) + F_2(g)$$

Equimolar mixtures of the solid reactants were heated in air at temperatures from 900 to 1100 °C. X-ray analyses of the products indicated that at least some uncombined MgO was present. This could have resulted from the oxidation of MgF_2 by either oxygen or water vapor. The following thermodynamic calculations were carried out to determine which reactant was responsible for the MgO formation:

Reaction (1). $MgF_2(s) + 1/2\,O_2(g) \rightarrow MgO(s) + F_2(g)$

Assuming $\Delta C_p = 0$, we can write

$$\Delta F^o_{1200\,^oK} = \Delta H^o_{298\,^oK} - 1200\,\Delta S^o_{298\,^oK} = 100{,}050 \text{ cal},$$

$$\log K = \Delta F^o/4.576T = -18.3,$$

and

$$P_{F_2} = K\,(P_{O_2})^{1/2} = 5\times10^{-19}(0.2)^{1/2} = 2.25\times10^{-19} \text{ atmos.}$$

Reaction (2). $MgF_2(s) + H_2O(g) \rightarrow MgO(s) + 2HF(g)$

For Reaction (2) we have

$$\Delta F^o_{1200\,^oK} = 12{,}950 \text{ cal}$$

and

$$\log K = -2.36.$$

Air at 25 °C and 50% relative humidity has a P_{H_2O} of 1.6×10^{-2} atmos. Thus we obtain

$$P_{HF} = (KP_{H_2O})^{1/2} \cong 8\times10^{-3} \text{ atmos.}$$

On comparison of the partial pressures of F_2 and HF produced by Reactions (1) and (2) respectively, it is evident that the water vapor reaction is more probable. Comparative weight-loss runs confirmed that MgF_2 was oxidized much more rapidly with water vapor than with dry oxygen. Therefore, this investigation was concerned with the more important water-vapor reaction.

The formation of MgO from MgF_2 involves a weight loss of about 35%. Thus, the progress of the reaction can be followed with a high-temperature weight-change apparatus. This reaction is also desirable for study because there are no known intermediate reaction products to complicate its interpretation.

The literature contains little information concerning the kinetics of high-temperature reactions involving gases and ionic or covalent solids. However, several general works that deal with related processes are available.

A good discussion of the determination of reaction order in gas-solid reactions is given in a monograph on the oxidation of metals by Kubaschewski and Hopkins.[1] Garner has surveyed the work on the endothermic decomposition of solids.[2] Except for the additional complicating step of the chemical reaction itself, these decompositions are quite analogous to the endothermic reaction dealt with in the present work. A discussion of factors that can lead to difficulties in the interpretation of the results of endothermic decomposition studies has been offered by Britton et al.[3]

Since the start of this study, a paper dealing with the hydrolysis of a number of fluorides, including MgF_2, has appeared in the literature.[4] A comparison of the activation energies reported and those obtained in this investigation emphasized the fact that sample geometry and physical state (polycrystalline, single-crystal, etc.) decidedly influence the results of such high-temperature kinetic studies.

II. EXPERIMENT

A. Materials

Three different types of specimens were used in the experimental determinations. These included powders, single-crystal cubes, and polycrystalline sintered discs.

The MgF_2 powder used for both the powder runs and fabrication of discs was provided by the U. S. Bureau of Mines Thermodynamics Group.* It was prepared by reacting MgO with hydrofluoric acid. The resulting MgF_2 was dried at 400°C. This material showed no weight loss after being heated to 600°C. Therefore, it was assumed that the absorbed water content was negligible. X-ray-diffraction patterns of this material revealed no detectable crystalline impurities.

The sintered polycrystalline discs were made by dry pressing in air and sintering in a dry argon atmosphere. Before pressing, the powder was ground to -200 mesh. Then, 0.5-g samples were dry-pressed at 5000 psi into discs 0.5 in. in diameter. These discs were sintered at 1100°C for three hours. Their surface areas were calculated from measurements made with a micrometer.

The single-crystal specimens were fabricated from material supplied by two sources. An infrared spectrograph on material furnished by W. Scott of this laboratory showed no detectable impurities. Additional material was obtained from A. Duncanson, Aberdeen University, Scotland. Specimens of known crystallographic orientation were made from pieces of material whose orientation had been previously determined from back-reflection Laue patterns. Cubes weighing approximately 0.5 g each were cut with a diamond saw and polished down to 3/0 paper. The orientations of the individual specimens were rechecked. The cubes were measured with a micrometer.

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*K. K. Kelley, Berkeley Thermodynamics Laboratory Region II Bureau of Mines, Berkeley 4, California.

B. Apparatus

The experimental apparatus used is shown in Fig. 1. The weight-loss measuring device consisted of a fused-silica helix from which the sample holder was suspended. The change in extension of the helix was determined by taking periodic readings with the cathetometer. In order to avoid errors due to thermal expansion of the apparatus, it was necessary to use a reference marker which was attached to the helix suspension point. This system gave weight-loss measurements with a precision of ±0.5mg.

Two different sample containers were employed. A platinum crucible was used for the powder runs, and a platinum mesh basket for single-crystal and disc runs. In each case, the container was suspended from the helix by 0.002-in. Ni wire.

The vertical-tube furnace was heated by a helical Kanthal-A winding. Its maximum operating temperature was 1200°C. A high-low temperature control provided by a Micromax controller was used to control temperature to ±5°C. Temperatures were measured with a $Pt-Pt_{90}Rh_{10}$ thermocouple whose output was read with a potentiometer. The reaction chamber consisted of a 1-1/4-in. o.d. mullite tube.

The atmosphere control system was patterned after that described by Datsur and Chipman.[5] A spherical float-type flowmeter was used to measure the gas flow rate. Water vapor and oxygen impurities were removed from the argon by the drying train and heated copper chips. The water-vapor partial pressure was controlled by setting the thermostat at the desired temperature. The saturated argon stream then possessed an amount of water vapor proportional to the vapor pressure of water at the temperature of saturation. The saturator bottles contained glass beads to insure dispersion of the carrier gas. The output trap was filled with glass wool to prevent spray from entering the heated tubing. A glycerine bubbler at the furnace output prevented back-diffusion into the system. With this bubbler arrangement, the pressure in the system remained at approximately 1 atmos.

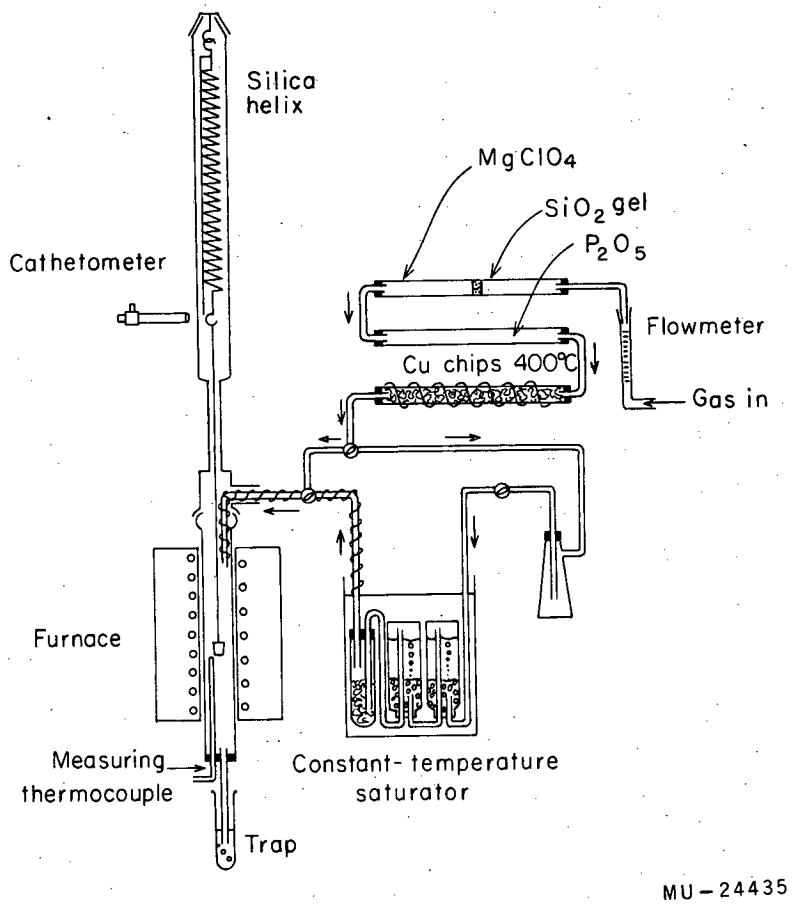

Fig. 1. High-temperature weight-loss balance system.

During the runs, time intervals were measured with a stop watch.

Various supplementary items of equipment were employed in the examination of the specimens. These included stereo and metallographic microscopes. An Orthopot macro-camera was used to obtain photomicrographs of sections of the reacted specimens.

C. Procedure

The procedure for experimental runs varied only in the method used for sample preparation. The powder samples were prepared simply by weighing 0.5-g amounts of MgF_2 powder into the platinum crucible. The single-crystal and disc specimens were placed in the platinum basket. Their exact weights were found by difference weighing with an analytical balance.

All runs were made at a water-vapor partial pressure of 55.3 mm. The gas flow rate was set at 285 cc/min. In order to determine whether the results would change, several runs were made with a flow rate of 190 cc/min. No significant differences were noted.

The procedure for making the runs was as follows:

(a) The sample container was suspended from the helix into the reaction chamber.

(b) The sample was heated to the desired test temperature in dry argon.

(c) The argon stream was diverted to pass through the saturator. This operation initiated the reaction, and the timer was started.

(d) The helix extension was read at regular intervals whose length depended upon the reaction rate at the selected test temperature.

After reaction, specimen surfaces and cross sections were examined with the microscope. X-ray diffraction was used to identify the reaction product. Back-reflection x-ray patterns of the single-crystal specimens were used in an attempt to establish the orientation of the MgO in the product layer.

III. RESULTS

A. Determination of Weight Loss

The reaction between MgF_2 and water vapor was found to proceed quite rapidly in the temperature range from 950 to 1100 °C. At 1100 °C, the reaction went to about 50% completion in two hours. The results of the weight-loss vs time runs for powdered, polycrystalline disc, and single-crystal samples are given in Figs. 2, 3, and 4. In accordance with the equations to be derived below, the fraction of MgF_2 remaining, w/w_0, was taken as a measure of the extent of reaction. All determinations were made with a water vapor partial pressure of 55.3 mm.

Because of a scarcity of material, samples of different sizes had to be used for the single-crystal runs. Therefore, the curves in Fig. 4 cannot be directly compared. However, as indicated further on in the text, the procedure employed for the determination of rate constants takes this size factor into account.

B. Derivation of a 2/3-Order Rate Equation

The reaction proceeded through the formation of an MgO coating on the MgF_2. As this coating increased in thickness, the volume of the remaining MgF_2 core, and consequently its surface area, decreased. Since the reaction rate depends upon the surface area of the unreacted material, equations were derived to allow for this continuous area change. For all of the geometric shapes considered, this area change consideration resulted in equations which show that the reaction rate is proportional to the 2/3 power of the weight of MgF_2 remaining.

In the following derivations, two assumptions were made. First, it was assumed that reaction rate is proportional to the surface area of the remaining unreacted material. Second, it was assumed that the product layer was of uniform thickness. Thus, the relative dimensions of the unreacted portion remain constant.

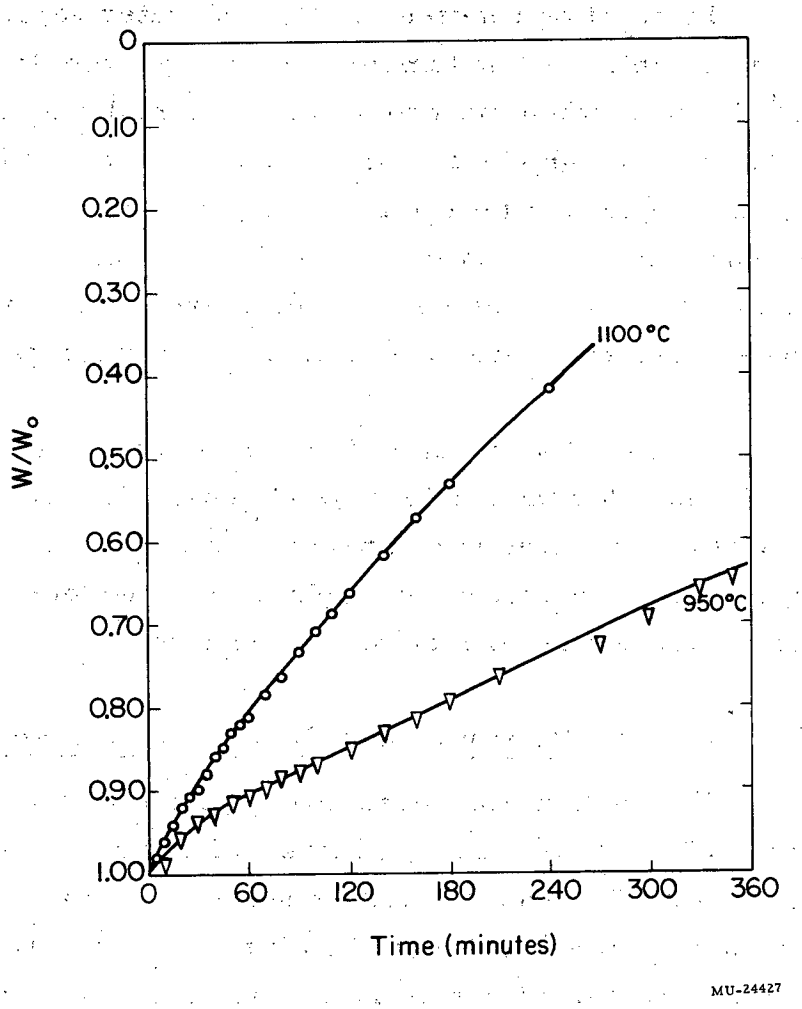

Fig. 2. Plot of w/w_0 vs t for powder specimens.

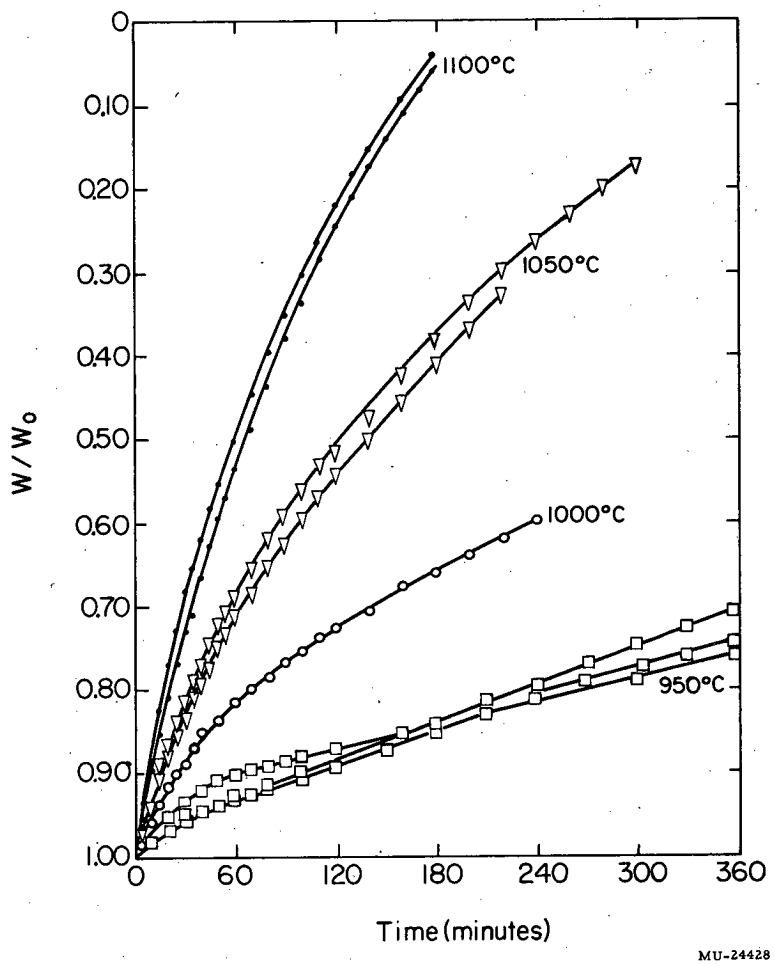

Fig. 3. Plot of w/w_0 vs t for polycrystalline discs.

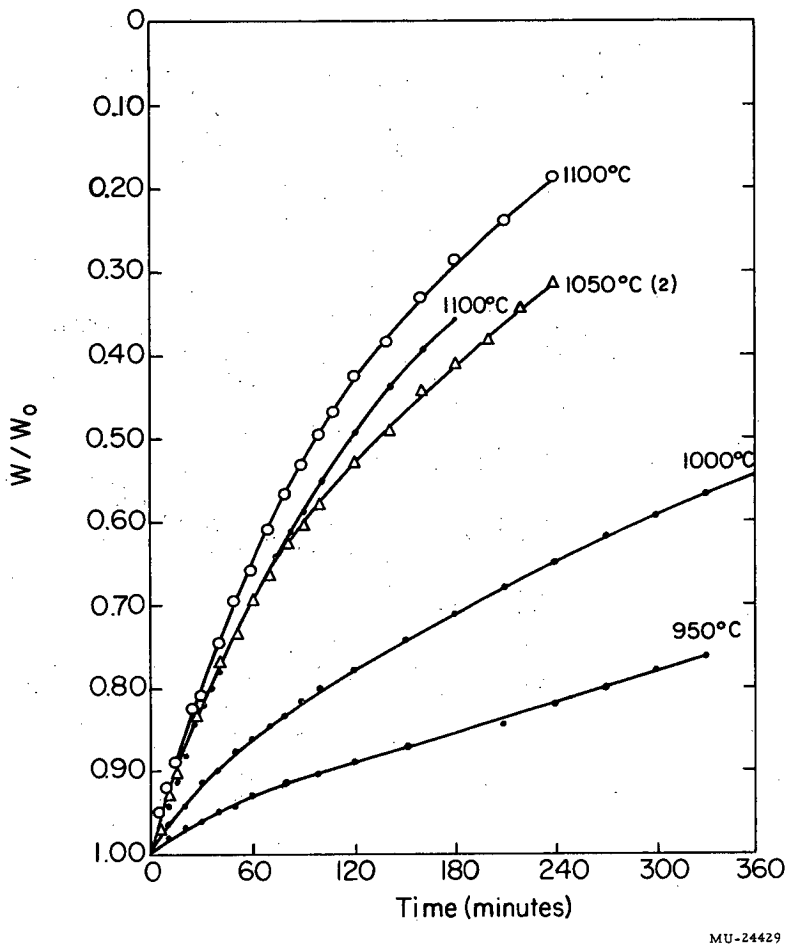

Fig. 4. Plot of w/w_0 vs t for single-crystal cubes.

For cylindrical specimens we can write

$$dw/dt = - k' A, \qquad (1)$$

where t is time, w is the weight of unreacted material, A is the surface area of unreacted material, and k' is a constant.

For a cylinder of height h and diameter d, assuming a uniform product layer, we have

$h/d = c$, where c is a constant. For radius r the volume is

$$V = \pi r^2 h = 2c\pi r^3,$$

the area is

$$A = 2\pi r^2 + 2\pi rh = 2\pi r^2 + 4c\pi r^2 = 2\pi r^2(1+2c)$$

and we have

$$V^{2/3} = 2^{2/3}\pi^{2/3}c^{2/3}r^2 .$$

Eliminating r, and expressing A in terms of V, we have

$$A = \frac{(2c+1)\pi^{1/3}2^{1/3}V^{2/3}}{c^{2/3}} = 1.85\left(\frac{2c+1}{c^{2/3}}\right)\left(\frac{w}{\rho}\right)^{2/3},$$

with

$$V^{2/3} = \left(\frac{w}{\rho}\right)^{2/3} \quad \text{where } \rho \text{ is the density.}$$

$$A = 1.85\left(\frac{2c+1}{c^{2/3}}\right)\left(\frac{w}{\rho}\right)^{2/3}$$

Let

$$\left(\frac{2c+1}{c^{2/3}}\right) = B.$$

Then we can write

$$\frac{dw}{dt} = - k' A = - 1.85\, k'\, B \left(\frac{w}{\rho}\right)^{2/3} .$$

Integrating the preceding expression over the time interval $(t_2 - t_1)$, we have

$$w_{t_1}^{1/3} - w_{t_2}^{1/3} = - \frac{0.617\, k' B\, (t_2 - t_1)}{\rho^{2/3}} , \qquad (2)$$

or, collecting constant terms,

$$w_{t_1}^{1/3} - w_{t_2}^{1/3} = - k\, B \Delta t . \qquad (3)$$

At $t = 0$, w is equal to w_0. Substituting and dividing through by $w_0^{1/3}$, we have

$$\left(\frac{w}{w_0} \right)^{1/3} = 1 - \frac{kB\Delta t}{w_0^{1/3}} . \qquad (4)$$

The above equations were applied to the powder and disc specimen data. This procedure was justified for the powder specimens because, by sintering to about one-fourth of their original sizes, they became compacts which retained the shape of the cylindrical platinum crucible. Thus they were effectively cylinders whose bases rested on the bottom of the crucible and whose tops and sides were exposed to the attacking atmosphere.

A similar derivation was carried out for the single-crystal specimens. These were either cubes of edge length ℓ, or parallelopipeds with one square cross section and height h. Letting $h = c\ell$, we obtain the integrated rate equation

$$w_{t_1}^{1/3} - w_{t_2}^{1/3} = - \frac{2}{3} \left(\frac{1+2c}{c^{2/3}} \right) \frac{k'}{\rho^{2/3}} \Delta t . \qquad (5)$$

Again, letting $\left(\frac{1+2c}{c^{2/3}}\right) = B$ and collecting constants,

$$w_{t_1}^{1/3} - w_{t_2}^{1/3} = - kB\Delta t . \qquad (6)$$

For a perfect cube, B equals 3. For other specimens, this quantity was obtained from micrometer measurements.

C. Application of the 2/3-Order Equation to Weight-Loss Data

If the reaction rate depends solely upon the surface area of the unreacted material, Eq. (4) shows that a plot of $(w/w_0)^{1/3}$ vs time should be linear. Figure 5 gives a typical plot using the single-crystal data for four runs at different temperatures. Plots of the data for other specimens were similar. It is evident that, following initial curved portions, the plots became linear.

Experimental points from the straight line portions of the $(w/w_0)^{1/3}$ vs time curves were used in calculating rate constants. The calculations and values obtained for rate constants of the powder, disc, and single-crystal specimens are given in Tables I, II, and III. The procedure was consistent for calculation of these values for a given set of specimens. However, because of differences in sample size, shape, and porosity, the rate constants for different sample types cannot be directly compared.

D. Determination of the Activation Energy

Figure 6 is a plot of the rate data for each of the three sample types according to the Arrhenius equation:

$$k = A\, e^{-E^*/RT}$$

$$\ln k = \ln A - E^*/RT$$

Activation energies were obtained from the slopes of the plots of ln k vs 1/T. The least-squares slopes were used for the single-crystal and disc specimens. An error analysis was made according to the method given by Benson.[6] The following activation-energy values were obtained:

Specimen type	E^* (kcal/mole)
Powder	25
Polycrystalline disc	56.1±6
Single crystal	42.3±5

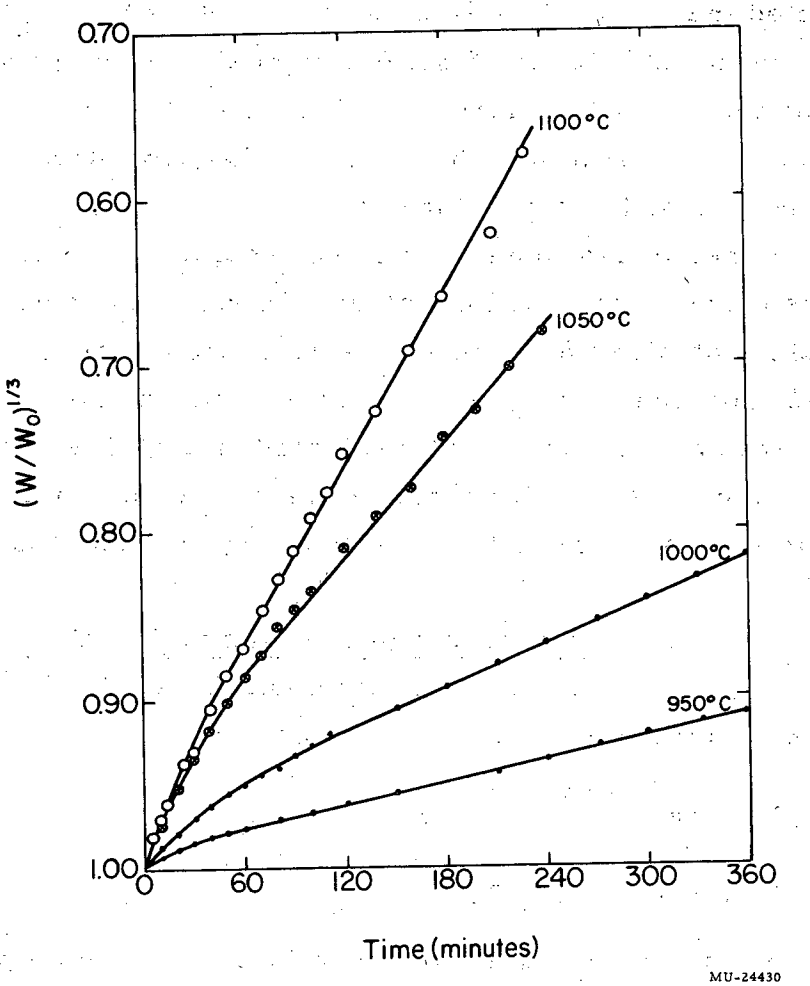

Fig. 5. Plot of $(w/w_0)^{1/3}$ vs t for single-crystal cubes.

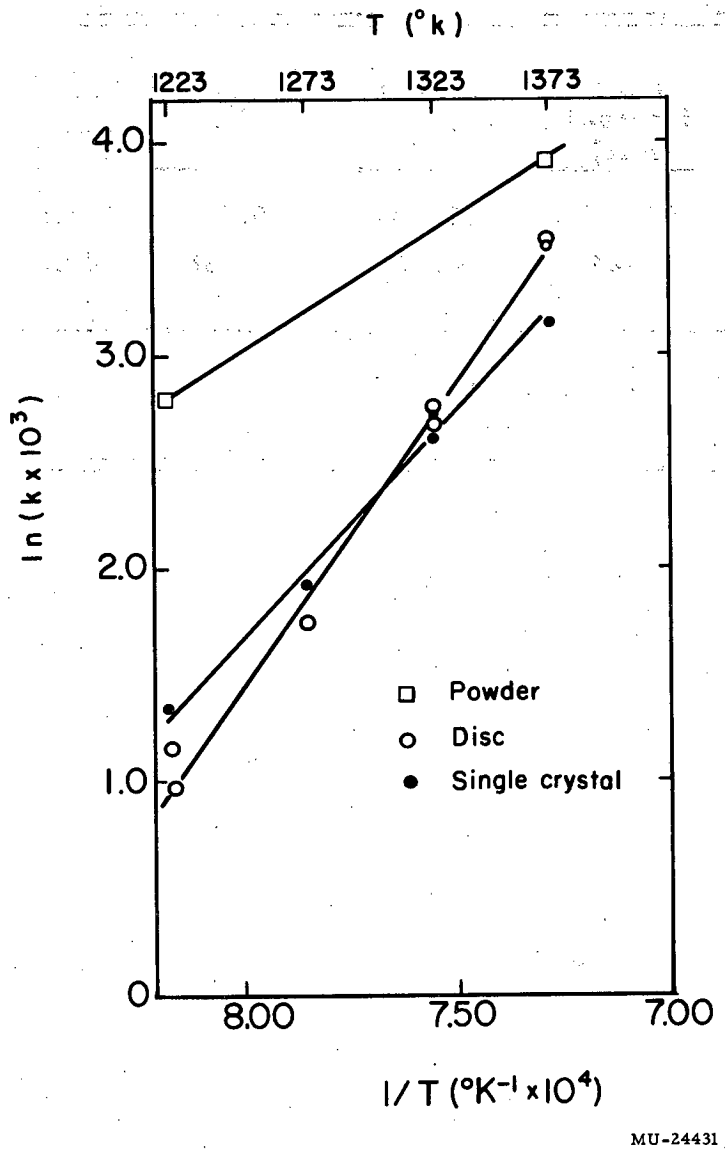

Fig. 6. Plot of ln $(k \times 10^3)$ vs T and 1/T for various specimens.

Table I. Calculation of rate constants for powder samples[a]

Temp. (^{o}K)	Time interval (min)	$w_{t_1}^{1/3}$	$w_{t_2}^{1/3}$	$k \times 10^3$ per hr	$\ln(k \times 10^3)$
1223	60-180	0.762	0.729	16.5	2.80
1373	60-240	0.734	0.588	49.0	3.90

a $w_{t_1}^{1/3} - w_{t_2}^{1/3} = - k (t_2 - t_1)$.

Table II. Calculation of rate constants for polycrystalline-disc samples[a]

Temp. (°K)	Run No.	Time interval (min)	$w_{t_1}^{1/3}$	$w_{t_2}^{1/3}$	B	$k \times 10^3$ per hr	$\ln(k \times 10^3)$	avg. $\ln(k \times 10^3)$
1223	1	60-240	0.757	0.707	4.13	2.02	0.70	
1223	2	60-360	0.762	0.696	4.17	3.17	1.15	0.94
1223	3	60-360	0.761	0.705	4.24	2.64	0.97	
1273		60-240	0.731	0.659	4.24	5.66	1.74	1.74
1323	1	60-240	0.692	0.501	4.09	15.6	2.75	
								2.72
1323	2	60-250	0.698	0.508	4.14	14.5	2.68	
1373	1	30-100	0.689	0.525	4.17	33.8	3.51	
								3.52
1373	2	40-100	0.685	0.544	4.12	34.2	3.54	

[a] $w_{t_1}^{1/3} - w_{t_2}^{1/3} = -kB(t_2 - t_1)$

Table III. Calculation of rate constants for single-crystal samples[a]

Temp. (°K)	Run No.	Time interval (min)	$w_{t_1}^{1/3}$	$w_{t_2}^{1/3}$	B	$k \times 10^3$ per hr	$\ln(k \times 10^3)$	Avg. $\ln(k \times 10^3)$
1223	1	60-360	0.845	0.788	3	3.80	1.33	1.33
1273	1	120-360	0.711	0.631	3	6.67	1.91	1.91
1323	1	60-240	0.590	0.453	3.03	15.1	2.72	
								2.66
1323	2	100-280	0.566	0.444	3.03	13.4	2.60	
1373	1	60-140	0.692	0.594	3	24.6	3.20	
								3.17
1373	2	80-160	0.571	0.478	3.02	23.2	3.14	

[a] $w_{t_1}^{1/3} - w_{t_2}^{1/3} = -kB(t_2 - t_1)$

The two powder runs were made primarily for comparison with the results of other workers.[4] Since good agreement was obtained, no further determinations were made on powder specimens.

E. Microstructures of Reacted Specimens

Microscopic examination of sections of the reacted specimens showed that there was a clearly defined interface between reactant and product on all specimen types. The product adhered tenaciously to the reactant and showed no tendency to crack or fall off.

Figure 7 shows the microstructures of the product layers on different specimen types. It is evident that the product layer on the discs and powder specimens had a very fine-grained, practically amorphous appearance. On the other hand, the MgO coating on the single-crystal specimens had a platy habit. Figure 7 shows the typical appearance of the "plates". These were always found to be oriented perpendicular to to the MgF_2 surface.

The presence of anisotropy of reaction was suspected. However, examination of the thickness of the product layer in different crystallographic directions on the single-crystal specimens showed no significant variations.

F. X-ray Results

X-ray—diffraction patterns on pulverized reacted specimens showed only MgO and MgF_2 to be present.

The MgO coatings on the single-crystal specimens produced back-reflection Laue patterns typical of preferred orientation. Preliminary studies gave no evidence that there is a simple epitaxial relationship with the structure of the underlying MgF_2. It has been mentioned above that microstructure examinations indicated that there was a preferred growth pattern with respect to the MgF_2 surface, but further work will be necessary to accurately establish the orientation. Back-reflection patterns of the product layer on the polycrystalline disc specimens showed random orientation.

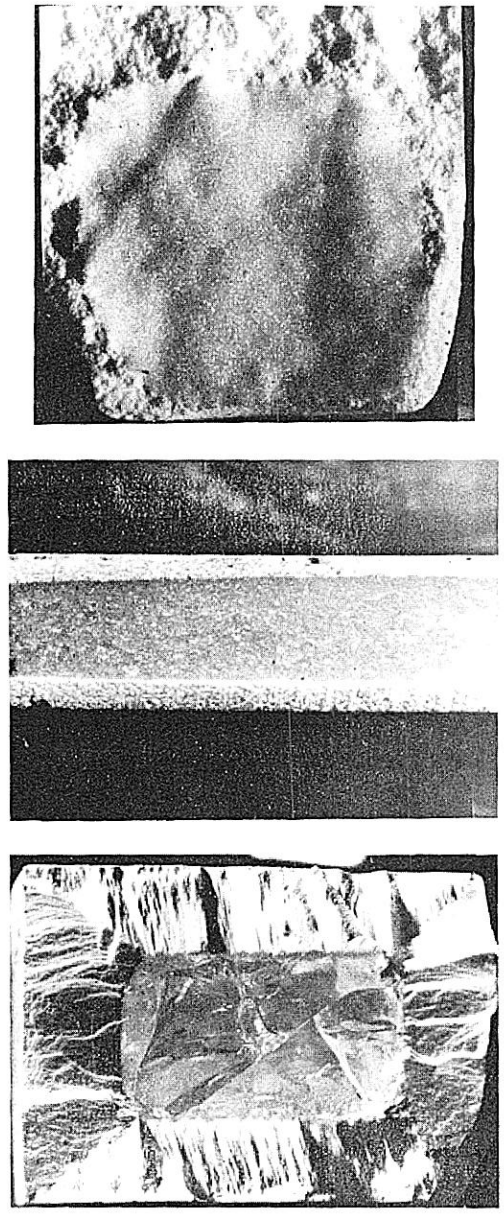

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Fig. 7. Microstructure of reacted specimen (×13). Top: powder; center: polycrystalline disc; and bottom: single-crystal specimen.

IV. DISCUSSION

It was stated in Section III that, in interface-controlled reactions, the reaction rate is proportional to the surface area of the unreacted material and consequently to the 2/3 power of the amount of unreacted material. Since the reaction rate is constant, and only the surface area changes, it seems justifiable to regard such a process as following zero-order kinetics. However, the common practice in the literature is to identify such behavior as 2/3-order kinetics, and such a description is used in the following discussion.

In the evaluation of the kinetics of reactions in which the product forms a coating on the reactant, the Piling-Bedworth ratio must be considered. This quantity, the ratio of the specific volumes of product and reactant, is equal to 0.57 for MgO/MgF_2. Such a large volume difference would be expected to induce great strains in the product layer, and possibly cause cracking in it. Although no large cracks were observed in the MgO product layer, it seems likely that micro-cracking must have been present at the interface.

The over-all sample size of both the disc and single-crystal specimens did not change during the reaction. Micrometer measurements showed that the dimensions of the reacted specimens were within 1% of their initial values. This indicated that the MgO was highly porous. Such a porous layer would not be expected to provide much protection for the underlying MgF_2 surface.

In the results, the presence of a clearly defined interface was given as evidence that the changing surface area of the specimen had to be taken into account. If, for the reasons advanced above, the product layer was nonprotective and the weight-loss data were plotted according to a 2/3-order rate law, the resulting curves should be linear. Any deviations from 2/3-order kinetics should be evident in departures from linearity in the plot of the integrated form of the 2/3-order rate equation. Figure 5 indicates that, after an initial deviation from linearity, a steady state is reached where this rate law appears to be valid. The extent of

reaction corresponding to the beginning of the linear portion of the plot varied from about 30% at 1100°C to 10% at 950°C.

This initial deviation could have been due to several causes. First, one would suspect that even a very porous coating would offer some impedance to the flow of reactant and product gases. However, the evaluation of such effusion effects is complicated by their dependence upon the exact size, shape, and length of the pores. Since these factors were unknown for the MgO product layers, any effusion effects can only be characterized qualitatively.

One could attempt to establish the presence of effusion by the determination of its temperature dependency. However, here again the temperature coefficient depends upon the nature of the pores. This coefficient can range from negative values for Poiseuille flow in large pores to positive values where Knudsen flow occurs. Regardless of the type of effusion taking place, one would anticipate that the impedance to flow would be directly proportional to the thickness of the product layer, resulting in a parabolic rate law. A test of the experimental data showed that they did not fit such a law.

There is a further possibility that the deviation from linearity could have resulted from a pressure build-up inside the sample. In the early stages of the reaction, this layer would be thin, and the gaseous product could escape easily. As its thickness increased, the apparent reaction rate would decrease because of the increasing difficulty of escape of the product gas. Thus, the pressure would build up until an equilibrium was reached between the rate of escape of the gas and the rate of reaction. This could result in the steady state suggested by the linear portions of the curves in Fig. 5. After a steady state was obtained, such a mechanism would not involve a dependency upon the thickness of the product layer. Furthermore, since the rate of escape of the gas would be proportional to the reaction rate, the rate constants obtained would still be accurate measures of the velocity of the chemical reaction.

In endothermic reactions, the probable occurrence of the back reaction must be kept in mind. If one considers a possible pressure buildup such as that described above, it seems likely that some of the HF would recombine in its passage through the product layer. However, if this process were rate controlling, the amount of recombination should be proportional to the thickness of the product layer, and a parabolic law would result.

It appears that all of the above-mentioned factors, although not strictly rate-controlling individually, could contribute to the initial deviation from 2/3-order kinetics.

Although it is difficult to estimate an activation energy accurately, one can obtain an idea of its approximate magnitude for an endothermic reaction. For such a reaction, it should be at least equal to the heat of reaction. For the reaction between MgF_2 and water vapor, ΔH_{1200^oK} is 43.8 kcal per mole. The single-crystal value of 42.3±5 kcal per mole is in good agreement with this figure. Garner has tabulated the results of a number of endothermic decompositions where similar agreement was obtained between heat of reaction and activation energy.[3] The polycrystalline-disc value of 56.1±6 kcal per mole is substantially different, but still greater than the heat of reaction.

The single-crystal result indicates that the controlling step is the chemical reaction itself. The higher value calculated from the polycrystalline-disc data indicates that the temperature dependence of the rate is influenced by additional factors. Figure 7 shows that the microstructure of the MgO layer on these specimens differed considerably from that on the single-crystal specimens. The coating on the latter appeared to have long channels between the plates and perpendicular to the MgF_2 surface. On the other hand, the coating on the discs gave no evidence of preferred pore orientation. Such a random structure would probably offer a greater amount of resistance to the flow of gases. The effect of this resistance might be overcome by increased molecular velocity at the higher temperatures. Thus, a greater reaction-rate temperature dependency and higher activation-energy value would result.

Since the initiation of this study, Deadmore et al. have reported an activation energy for this reaction.[4] The two powder runs were made in an effort to duplicate Deadmore's reported results. The value of 25 kcal per mole obtained in this investigation is in good agreement with the reported figure of "about 21 kcal per mole", but much lower than the values for the single-crystal and disc specimens. The explanation for this discrepancy undoubtedly lies in the fact that MgF_2 powder sinters quite readily in the temperature range being considered. For samples of equal weight sintering decreases the surface area to a greater extent at 1100°C than at 950°C, thereby causing a reduction of the measured reaction rate at the higher temperature relative to the lower one. The apparently low activation energy was a result of this process.

The preceding discussion emphasizes the great important of considering physical factors in dealing with high-temperature reactions similar to the one studied. In the present case, it is evident that the previous treatment and state of aggregation of the reactant radically altered the observed kinetics.

Although single-crystal specimens of two different orientations were used, a comparison of reaction rates revealed no detectable anisotropy. In addition, inspection of a section of a cube whose faces were approximately (001) and (110) showed that the thickness of the product layer was the same on the two faces.

It was mentioned that the MgO layer on the single-crystal specimens showed preferred orientation. The Laue patterns indicate that this layer resembles a polycrystalline material with a texture rather than a pseudo single crystal. Therefore, it is difficult to establish whether a simple epitaxial relationship exists between reactant and product. It is anticipated that future studies of the structural details of the product layer and interface will help in the understanding of the role they play in influencing the kinetics of this reaction.

V. SUMMARY

In summary, it may be concluded that:

(a) After the attainment of steady-state conditions, the reaction between MgF_2 and water vapor follows a 2/3-order rate law.

(b) The activation energy of 42.3±5 kcal per mole obtained with the single-crystal specimens agreed quite well with the heat of reaction of 43.8 kcal per mole. Therefore, it was concluded that the rate-controlling step was the chemical reaction itself.

(c) The low value of 25 kcal per mole for the powder specimens and the high figure of 56.1±6 kcal per mole for the sintered polycrystalline discs were due to microstructural features in these specimens. Sintered interfered in the case of the powder specimens. The structure of the product layer on the discs was such as to provide a greater impedance to gas flow than was given by the single-crystal product layer.

(d) The above conclusions emphasize the great importance of considering the physical state of specimens used in studying high-temperature gas-solid reactions.

VI. ACKNOWLEDGMENT

Grateful acknowledgment is extended to Mr. Reuben R. Hammer for his assistance in initiating this study. The author also wishes to thank Professor Joseph A. Pask for his guidance and helpful suggestions. This work was done under the auspices of the U. S. Atomic Energy Commission and the Office of Naval Research.

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